PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 53/56, F23J 15/02 | A1

(11) International Publication Number: WO 98/03249

(43) International Publication Date: 29 January 1998 (29.01.98)

(21) International Application Number: PCT/DK97/00315

(22) International Filing Date: 18 July 1997 (18.07.97)

(30) Priority Data:
0804/96 22 July 1996 (22.07.96) DK

(71) Applicant (*for all designated States except US*): FLS MILJØ A/S [DK/DK]; Ramsingsvej 30, DK-2500 Valby (DK).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): BOSCAK, Vladimir [US/DK]; Ramsingsvej 30, DK-2500 Valby (DK).

(74) Agent: HOFMAN-BANG & BOUTARD, LEHMANN & REE A/S; Hans Bekkevolds Allé 7, DK-2900 Hellerup (DK).

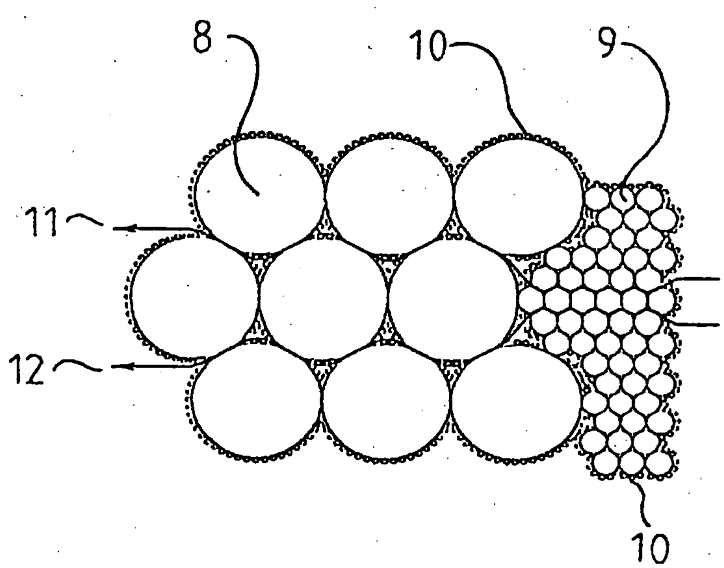
(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

**Published**
*With international search report.*

(54) Title: FLUE GAS CLEANING DEVICE WITH CATALYTIC CERAMIC FILTER

(57) Abstract

The invention relates to a flue gas cleaning device (1) comprising a porous filter structure, said structure having a first and a second face where the pores of the porous structure form passages for flue gas between said first and second faces and jointly comprising a catalyst material for selective catalytic reduction of $NO_x$ in the presence of ammonia, where this catalyst material (10) is applied on the surface of the passages. Hereby an improved $NO_x$ removal is obtained. The invention further relates to a flue gas cleaning system and a method for flue gas cleaning utilizing such a device where removal of all pollutants in the flue gas is possible. Still further the invention relates to a method of manufacturing the device.



*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | | TR | Turkey |
| BG | Bulgaria | HU | Hungary | ML | Mali | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MN | Mongolia | UA | Ukraine |
| BR | Brazil | IL | Israel | MR | Mauritania | UG | Uganda |
| BY | Belarus | IS | Iceland | MW | Malawi | US | United States of America |
| CA | Canada | IT | Italy | MX | Mexico | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NE | Niger | VN | Viet Nam |
| CG | Congo | KE | Kenya | NL | Netherlands | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NO | Norway | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | NZ | New Zealand | | |
| CM | Cameroon | | | PL | Poland | | |
| CN | China | KR | Republic of Korea | PT | Portugal | | |
| CU | Cuba | KZ | Kazakstan | RO | Romania | | |
| CZ | Czech Republic | LC | Saint Lucia | RU | Russian Federation | | |
| DE | Germany | LI | Liechtenstein | SD | Sudan | | |
| DK | Denmark | LK | Sri Lanka | SE | Sweden | | |
| EE | Estonia | LR | Liberia | SG | Singapore | | |

Flue gas cleaning device with catalytic ceramic filter.

The present invention relates to a flue gas cleaning device of the type set forth in the introductory part of claim 1.

The emission standards for fossil fuel power plants regulate three pollutants that have to be controlled; particulate matter, $SO_2$, and $NO_x$. These pollutants are as a rule controlled by the dedicated technologies; particulate matter by electrostatic precipitators, fabric filters, or porous ceramic filter. $SO_2$ by Flue Gas Desulfurization systems (primarily wet scrubbers) and $NO_x$ by Selective Catalytic Reduction or Selective Non Catalytic Reduction technologies.

The standards for emissions from municipal, hazardous and clinical waste incineration plants cover several pollutants which can be divided into four categories: particulate matter, acid gases, heavy metals and dioxins. The cleaning of flue gases from waste incinerators is currently practised by the variety of generic and proprietary techniques for removal of particulate matter and gaseous pollutants. The most common techniques for particulate matter removal are fabric filters and electrostatic precipitators, while the gaseous pollutants are removed in the variety of dry, semi-dry and wet scrubbing techniques or their combination, using calcium or sodium reagents. More recently $NO_x$ is controlled by the Selective Non-Catalytic Reduction (SNCR) or the Selective Catalytic Reduction (SCR).

The ceramic filters, also called candle filters, can generally be divided into high and low density types. The high density types are made primarily of the following compounds: quartz ($SiO_2$), mullite ($3\ Al_2O_3 \times 2\ SiO_2$), aluminium oxide ($Al_2O_3$) and silicon carbide (SiC). The low density

types are typically made of alumina silica fibers. While the low density filters have a porosity of up to 90 %, the high density types have typical porosity of 40 %. The low density filters are characterized by low weight and low pressure drop, but show low strength sensitivity toward moisture and corrosion, and are only applicable to medium high temperature.

The high density filters which are more relevant to this invention are characterized by high removal efficiency and applicability to high temperature.

The pressure drop through ceramic filter is dictated by pore size and filter wall thickness. The relationship between pressure drop and gas velocity changes with length of in-service time. The change in pressure drop between subsequent filtering and cleaning cycles approaches zero as the total number of cycles increases, provided gas velocity remains constant. After about 200 cycles, ceramic filters have been observed to reach an equilibrium. The point of equilibrium depends on process conditions, ceramic composition, particulate matter characteristics, etc.

$NO_x$ in the flue gas can in general be controlled by the following methods:

* Use of low-nitrogen fuel
* Combustion modification:
  flue gas recirculation
  low $NO_x$ burners
  staged-air combustion
* Add-on $NO_x$ control:
  selective catalytic reduction (SCR)
  selective noncatalytic reduction (SNCR)

SCR is based on the ammonia injection into the flue gases in the presence of a catalyst to reduce NO and $NO_2$ to nitrogen and water:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

$$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O$$

The degree of $NO_x$ conversion depends on the temperature and amount of ammonia added. With increasing $NH_3/NO_x$ ratio conversion increases but one should prevent $NH_3$ slippage. By using a suitable catalyst more than 90 % reduction of $NO_x$ can be obtained at an $NH_3/NO_x$ molar ratio of approximately one within the temperature range of 300-400 °C.

The suitable catalyst carriers for SCR are characterized by:

* Low pressure drop
* High $NO_x$ removal efficiency
* Long lifetime
* Low $SO_2$ oxidation activity
* High tolerance to dust and other contaminants
* Resistance to thermal shocks
* High thermal stability

The carriers are typically based on the following compounds: titanium oxide, zeolite, iron oxide or activated carbon. Most commercial carriers use vanadium pentoxide as an active compound and titanium dioxide to disperse and support vanadia. They are monolithic in structure with a large number of parallel channels arranged in a honeycomb structure or in parallel plates. Plate types have generally higher resistance to erosion and deposition than honeycombs. The size of the channels depends on the flue gas particulate matter content and its characteristics. The

carriers can be tailormade to meet specific requirements regarding thermal stability or low activity towards $SO_2$ oxidation. The carriers are manufactured in standard elements, which can be assembled in large modules consisting of several elements facilitating the handling and installation of the catalyst carrier in the SCR reactor.

Until now $NO_x$ has been controlled in only few waste incineration plants by using SCR technique. An interesting finding in such applications was that dioxins emissions were also dramatically reduced.

In the prior art catalysts used in SCR techniques are normally applied to the surface of the plates that can have porous structure. The flue gas flows parallel to the plate at the rate of a couple of meters per second. The $NO_x$ reduction rates partly depend upon the rate at which the reactants diffuse through the wall of the porous catalyst to reach active sites where the reaction takes place. For NO reduction the rate of chemical reaction is fast relative to the rate of diffusion. Therefore, the catalyst is effective primarily at the surface of the wall.

In European patent application 242488-A a filter medium for treating an exhaust gas has a catalyst layer for eliminating nitrogen oxides formed on the other side of a porous ceramic substrate from which the exhaust gas is discharged. The filter medium may have a double-cylinder construction in which the catalyst layers formed on at least one side of an inner cylinder and the pre-coat layer and the solid material layer are formed on an outer side of an outer cylinder. This publication constitutes the closest prior art in relation to the present.

One control technology which is being demonstrated for simultaneous removal of $SO_2$, $NO_x$ and particulate matter in

fossil fuel power plants is SNRB ($SO_x$-$NO_x$-ROX BOX) covered by the US patents 4,309,386 and 4,793,981. In both patents the particulate matter and reaction products are removed by means of fabric filter. The catalyst for $NO_x$ removal is either added as a powder into the flue gas or is weaved into the fabric of the filter bags so that the catalyst is an integral component of the fabric.

The object of the present invention is to provide a flue gas cleaning device which, in relation to the closest prior art, allows for an improved $NO_x$ removal efficiency relative to the flue gas flow through the filter.

According to the invention this is obtained by a flue gas cleaning device of the type mentioned in the introductory part of claim 1 and which is characterized by the features set forth in the characterizing part of claim 1.

Providing the catalyst in the pores inside the porous filter structure allows for a more intimate contact betweeen the flue gas and the catalyst compared to devices where the flue gas flows parallel to a surface provided with a catalyst, and allows for a longer contact time compared to a device where the flue gas penetrates a layer of catalyst. This means that a combined particle and $NO_x$ removal unit with increased $NO_x$ removal efficiency and smaller dimensions than hitherto known is obtained. A simultaneous removal of dioxin, if present, is also obtained.

Advantageously, the porous structure has an essentially tubular shape where the first face extends along the outer circumference of the tube and the second face extends along the inner circumference of the tube.

In order to allow for a small cross section dimension between the first and the second faces of the tube, a sup-

porting structure, e.g. in the form of axially extending ribs, can be provided between opposing parts of the second face.

In order to improve removal efficiency of particulate matter in the filter, a membrane consisting of ultra fine sintered ceramic powder, e.g. SiC, can be applied onto the filter element surface.

The invention further relates to a system for cleaning flue gas wherein at least one duct is provided for leading the flue gas from a combustion chamber to the filter device housing and wherein means for injecting ammonia into said duct are provided.

The system may further comprise in said duct means for injecting sorbent or reagent for bringing $SO_x$, HCl or HF on a particulate form in order to allow a removal of these particles on the surface of the porous filter structure. Hereby a compact single unit cleaning system is provided.

The invention still further relates to a method for cleaning flue gas by use of a device which is characterized in that ammonia is injected into the flue gas stream upstream of the device.

In order to remove $SO_x$, HCl or HF from the flue gas, a sorbent or reagent for converting the flue gas content of $SO_x$, HCl or HF to particulate form is injected into the flue gas stream upstream of the device in order to remove in the device these particles from the flue gas.

- Acid gases (HCl and $SO_2$) are neutralized by in-duct injection of $NaHCO_3$, $Ca(OH)_2$ or other sodium- or calcium-based sorbents. The resulting sodium or calcium salts are removed together with the particulate mat-

ter (fly-ash) in a CCF.

- $NO_x$ is removed by reaction with ammonia over the filter's catalytic structure where dioxins are prevented from being formed or are also destroyed. Depending on the flue gas $NO_x/SO_2$ ratio catalytic ceramic filter operates in the temperature range of 200-400 °C.

- If needed heavy metals and residual dioxins can also be removed by active carbon or some other sorbent injection.

The invention also relates to a method of manufacturing a device as set forth above starting with a porous ceramic filter structure having a desired shape and pore size, which method includes

1) preparing a liquid mixture comprising catalyst and binder in a desired concentration,

2) submerging the filter structure into the liquid mixture for a time sufficient for allowing the liquid mixture to penetrate the pores of the filter structure, and

3) drying and hardening the filter structure with the applied catalyst and binder.

In the following an embodiment of the invention will be explained with reference to the drawing, where:

Figure 1 schematically shows in section a filter structure according to the invention attached to a supporting structure,

Figure 2 schematically shows in section an enlarged view of a part of the filter structure of Figure 1, and

Figure 3 schematically shows a system utilizing a device according to the invention.

Figure 1 represents the preferred embodiment of the catalytic ceramic filter (CCF) element 1 with a tubular shape and it illustrates one arrangement for holding the said element to the filter housing. Filter element is closed with the flat plate 2 on one side and has a flat flange 3 on the other end which is sealed by ceramic gasket 4 between clamp and spigot plate 5,6. A more detailed description of CCF arrangement will be given in the description of Figure 3. Depending on the flue gas characteristics and specific application requirements two basic types of CCF can be used. If one desires low pressure drop and requirements for $NO_x$ removal are not very demanding, a thin wall filter element with internal suppport ribs can be used. If high $NO_x$ (and dioxins) removal efficiencies are required and higher CCF pressure drops are of secondary importance, a thick wall filter element can be used. A thick wall element requires no supporting ribs.

Figure 2 shows the schematic close-up of CCF wall. This close-up illustrates the use of ultra-fine silicon carbide sintered powder layer 9 (membrane) at the outside face of the wall of the filter element. Its use is optional, while it has the benefit of serving as a barrier for very fine particulate matter it adds to the filter's pressure drop. Figure 2 further shows a mono-molecular layer of SCR catalyst 10 attached to the sintered SiC powder. The preferred formulation of the catalyst is vanadia supported by titania but in principle any SCR catalyst which can be prepared in

solution for impregnation of SiC filter structure can be used. Examples of SCR catalyst are: zeolites, bauxite, alumina, sodium aluminate, iron spinel, hematite, alunite, anataze, dawsonite, spinel, siderite, manganite, melite, gothite, azurite. The flow path for the flue gas is indicated by arrows 11,12.

Figure 3 shows the preferred embodiment of the invention in a combustion-energy generating facility.

A combustion chamber 13 of a generic type is illustrated which in the case of fossil fuel power plant has either dry or wet bottom furnace with front wall, opposed wall, corner, tangential or other firing while in the case of waste incineration consist of grate furnace, rotary kiln or their combination. Type of fuel fired in the combustion chamber dictates the composition of the flue gas and plays an important role in the selection of reagent for acid gas control in the CCF and its operating temperature. The flue gas generated by combustion of fossil fuel, namely coal or heavy oil, is characterized by high $SO_2$ concentration (in the order of thousands mg/$Nm^3$), medium to high $NO_x$ concentration (in the order of hundreds mg/$Nm^3$), low HCl concentration (in the order of tens mg/$NM^3$), high particulate matter load, medium heavy metals concentration, and practically no dioxins. The flue gas from either municipal, hazardous or clinical waste incineration is characterized by high HCl concentration (in the order of thousands mg/$Nm^3$), low to medium $NO_x$ concentration (in the order of hundreds of mg/$Nm^3$), medium $SO_2$ concentration (low hundreds mg/$Nm^3$), medium or low particulate matter load, medium or high heavy metals concentration and presence of dioxins in the order of tens ng TEQ/$Nm^3$. The clinical waste incinerators are characterized by very high dioxins content. A boiler 15 is shown and thermal energy is recovered by high pressure 14 and low pressure 16 steam tubes e.g. for generation of

electric power in a turbine. In many waste incineration facilities steam or hot water is used for district heating but newer waste-to-energy installations also employ electric power generation. An optionally induced draft fan 17 can be used downstream from the boiler. Even through it is not shown in Figure 3, one should note that most of the combustion facilities today are equipped with a particulate matter control device, most frequently an electrostatic precipitator or more recently bag filter.

Most combustion facilities also employ economizer as a part of boiler or as a stand alone unit.

In the preferred arrangement flue gases exiting boiler or particulate matter control device with temperature of about 300°C are introduced into reactor 18 or directly into the duct leading into CCF housing 27 comprising the filter 28 constituted by several filter devices 1 according to the invention. The reactor is used in the case of high concentration of acid gases or in the case where very high removal efficiency is required. The first step in flue gas cleaning is acid gas control. $SO_2$ and HCl as well as HF are removed from the flue gas by neutralization with a dry alkali. The selection of alkaline reagent is dictated by the concentration of acid gases and desired degree of removal. In the case of low concentration and low removal requirements, the preferred reagent is lime due to its relatively low cost. Its type (CaO or $Ca(OH)_2$), particle size distribution, addition of promoters, etc., is selected on the basis of the particular application. In the case when the acid gases concentration is high or the desired removal efficiency is high, sodium bicarbonate or carbonate is the reagent of choice, e.g. trona or nacolite. In the case of sodium based reagent on can again select its grind and other characteristics based on the particular application.

A combination of the reagents can also be used. One should here note that HCl and in particular HF are much easier removed than $SO_2$. For the same reason the reactor is used preferentially in the case of high $SO_2$ concentration as is the case for the flue gases from fossil fuel combustion facilities. The role of reactor is to provide intimate contact between reagent and acid gases so it may have some internals to enhance mass transfer. The reagent is stored into silo 20 from where it is injected into reactor via pipe 19. The reagent is transported pneumatically by the use of fan 21. In case there is no need for reactor, the reagent is injected directly into ductwork leading to CCF. In addition of gas-entrained reagent solids reaction, the removal of acid gases also takes place as the gas flows through the cake on CCF elements. The products of acid gases neutralization are calcium or sodium salts which together with unreacted reagent and fly ash are collected on the ceramic filter. The removal of residue takes place during the cleaning cycle.

Catalytic ceramic filter housing 27 is typically manufactured from mild steel plate of continuously welded and flanged construction and is designed to accomodate thermal expansion. The catalytic ceramic filter elements are sealed against the spigot plate 5 by a clamping plate 6. A ceramic gasket 4 is fitted between the spigot plate 5 and element flange 3 to ensure a good seal.

Each element is supported at the far end by support collars which form part of the filter casing. The pipe 29 for compressed air run vertically down each row of elements passing through the filter case at the top of the filter housing and connecting to the diaphragm valves 24 and compressed air manifolds. In the case support ribs are used in the elements, it is essential that the hole for jet pulse air injection is located precisely above the center of the ele-

ment. To enhance good jet pulse distribution, air is injected via venturi 7 shown in Figure 1. Pulse controller units and solenoid valves 30 enclosure, pre-wired, are also mounted on the filter top plate. The compressed gas is stored into a tank 31 connected to a pipe manifold.

Flanged inlets to the filter section are fitted to the top plate which provides "down flow" characteristics within the filter body thus assisting dust release in the hoppers. The complete top section is mounted on a valley type hopper equipped with a rotary valve 32, screw conveyor and dust collection bin discharge arrangement 33. The reaction chamber is designed to give a low velocity on each pass and give arduous route and dwell time for the gas flow, to ensure a good contact between the reactant and gas. The complete filter and hopper assembly is mounted on a substantial support structure, designed to give 1500 mm clearance under the rotary valve.

The new catalytic ceramic filter elements are conditioned during the first reverse pulse cleaning cycles. In this period a layer of dust builds up on the surface of elements resulting in an increase in pressure drop. Pressure drop equilibrium is reached rapidly after these initial cycles and afterwards the conditioned layer of dust provides for superefficient filtration. The ceramic elements can easily handle high face velocities so sudden volume changes present no problem.

In the case that residue from CCF is not acceptable for deposit it can be treated 38 to meet desired specifications. In the residue treatment one can employ resource recovery which depends on the reagent used. For example if reagent is calcium based, the resulting very soluble $CaCl_2$ can be recovered in the evaporator and used as de-icing agent. The prevailing calcium sulfite can be oxidized to the high-

grade gypsum for use in wall-board or cement production. One can also employ recovery of sulfur through calcination and production of elemental sulfur via Claus process, production of sulfuric acid through oxidation of $SO_2$ to $SO_3$ and subsequent absorption and production of compressed $SO_2$ gas.

In the case of sodium based reagent one can use the residual sodium salts as a valuable by-product for chemical or pulp and paper industry.

$NO_x$ is reduced to nitrogen by reaction with ammonia in the presence of catalyst applied into CCF elements. The ammonia stored as a liquid in a tank is first mixed with air in ammonia preparation device 25 and is then introduced into reactor or directly into duct in front of CCF via injection nozzles 24 designed for good ammonia distribution. The temperature of CCF is dictated by the composition of flue gases and desired removal efficiency. In the case of flue gas with high $SO_2$ and specifically $SO_3$ concentration as is mostly the case with fossil fuel combustion, a CCF temperature above 350°C is desired to prevent formation of solid ammonium disulfate which may plug the ceramic filter. In the case of low $SO_3$ concentration and low NO removal requirements CCF temperature can be below 300°C.

The dioxins formed on the fly ash through de-novo synthesis are oxidatively destroyed in the presence of SCR catalyst. In the case where sorbents are used for heavy metals control dioxins will also be adsorbed on said active carbon particles.

Most of heavy metals are condensed on the solids in the flue gas and are removed from the gas stream with the residue. Since CCF temperature is relatively high, some more

volatile heavy metals, namely mercury and cadmium, may be a problem. In such case a suitable sorbent may have to be added to the flue gas in front of CCF. The sorbent stored in a silo 22 can via fan 23 be introduced into the same pipe where reagent is fed to the CCF system. The suitable sorbent is for example active carbon as such or treated with phosphorus or sulfur. Sodium sulfid can also be used in particular if the mercury content is high.

The clean gas exiting CCF can be introduced into an optional economizer 34 where the heat can be recuperated by heating the water in the tubes 35. The flue gas is preferentially moved through CCF via an induced draft fan 37 discharging the gas to a stack 36.

In table 1 the $NO_x$ removal efficiency is demonstrated for varying operation conditions of a filter made from ceramic particles. The face velocity, the temperature, and the ammonia stoichiometry are varied.

In the filter used for the table 1 results, the following characteristics are present:

| | | |
|---|---|---|
| Filter: | Particle material: | SiC |
| | Particle size: | 250 µm ($250 \cdot 10^{-6}$m) |
| Catalyst: | Material: | $V_2O_5/TiO_2$ |
| Binder: | Material: | Urea-formaldehyde |

TABLE 1: CCF TESTS WITH FLUE GAS

| Face velocity cm/s | Pressure drop, mm WG | Temperature °C | Ammonia flow rate, ml/min | NO conc, Inlet, ppm | NO conc, Outlet, ppm | Removal efficiency % | Ammonia slip ppm |
|---|---|---|---|---|---|---|---|
| 2.0 | 90 | 400 | 10 | 400 | 300 | 25 | 300 |
| 2.0 | 90 | 400 | 7.5 | 400 | 320 | 20 | 80 |
| 2.0 | 90 | 400 | 5 | 400 | 330 | 17.5 | 50 |
| 2.0 | 90 | 400 | 2.5 | 400 | 360 | 10 | 0 |
| 1.2 | 20 | 400 | 5 | 400 | 220 | 45 | |
| 1.2 | 20 | 400 | 2.5 | 400 | 220 | 45 | |
| 1.0 | 20 | 400 | 2.5 | 400 | 120 | 70 | 200 |
| 0.5 | 20 | 400 | 2.5 | 400 | 80 | 80 | |
| 1.2 | 20 | 380 | 5 | 400 | 220 | 45 | |
| 1.2 | 20 | 360 | 5 | 400 | 250 | 37.5 | |
| 1.2 | 20 | 340 | 5 | 400 | 260 | 35 | |

As it appears from the table, a NO removal efficiency of up to 80% has been obtained.

Claims

1. A flue gas cleaning device (1) comprising a porous filter structure, said structure having a first and a second face where the pores of the porous structure forms passages for flue gas between said first and second faces and jointly comprising a catalyst material for selective catalytic reduction of $NO_x$ in the presence of ammonia, characterized in that the catalyst material (10) is applied on the surface of the passages.

2. A flue gas cleaning device according to claim 1, characterized in that the porous structure has an essentially tubular shape where the first face extends along the outer circumference of the tube and the second face extends along the inner circumference of the tube.

3. A flue gas cleaning device according to claim 2, characterized in that a supporting structure, e.g. in the form of axially extending ribs, is provided between opposing parts of the second face.

4. A flue gas cleaning device according to claim 1-3, characterized in that the porous structure is made from ceramic particles or fibres.

5. A flue gas cleaning device according to claims 1-3 where the porous structure is made of ceramic particles, characterized in that the particles have a dimension in the range of 200-300 μm.

6. A flue gas cleaning device according to claims 1-5, characterized in that a layer of particles (9) providing a smaller pore size than the porous structure

between the first and the second face is applied onto that of said faces directed towards the flue gas stream to be cleaned, said particles preferably having a dimension in the range of 30-50 µm.

7. A system for cleaning flue gas utilizing at least one device according to any one of claims 1-6, characterized in comprising at least one duct or reactor forming a flow path for the flue gas to the filter device and means for injecting ammonia into said duct or said reactor.

8. A system according to claim 7, characterized in further comprising in said duct means for injecting sorbent or reagent for converting $SO_x$, HCl or HF to a particulate form.

9. A method for cleaning flue gas by use of a device according to any one of claims 1-6, characterized in that ammonia is injected into the flue gas stream upstream of the device.

10. A method according to claim 9, , characterized in that sorbent or reagent for converting the flue gas content of $SO_x$, HCl or HF to particulate form is injected into the flue gas stream upstream of the device in order to remove in the device these particles from the flue gas.

11. A method according to any of claims 9 or 10, characterized in that the temperature of the flue gas to be cleaned is within the range of 200°C-400°C immediately prior to the entrance of the porous structure.

12. A method of manufacturing a device according to any

one of claims 1-6, c h a r a c t e r i z e d in starting with a porous ceramic filter structure having a desired shape and pore size and comprising

1) preparing a liquid mixture comprising catalyst and binder in a desired concentration,

2) submerging the filter structure into the liquid mixture for a time sufficient for allowing the liquid mixture to penetrate the pores of the filter structure, and

3) drying and hardening the filter structure with the applied catalyst and binder.

13. A method according to claim 12, c h a r a c t e r i z e d in that steps 2) and 3) are repeated until a desired catalyst layer thickness is obtained.

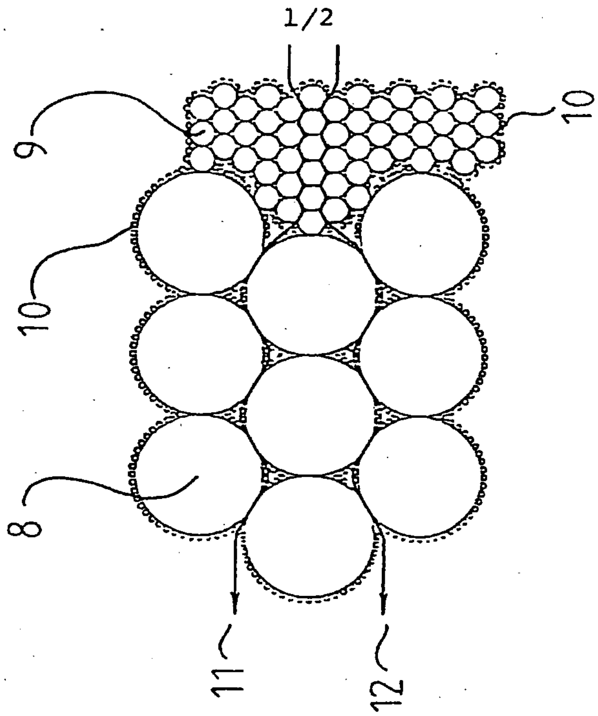



FIG. 2

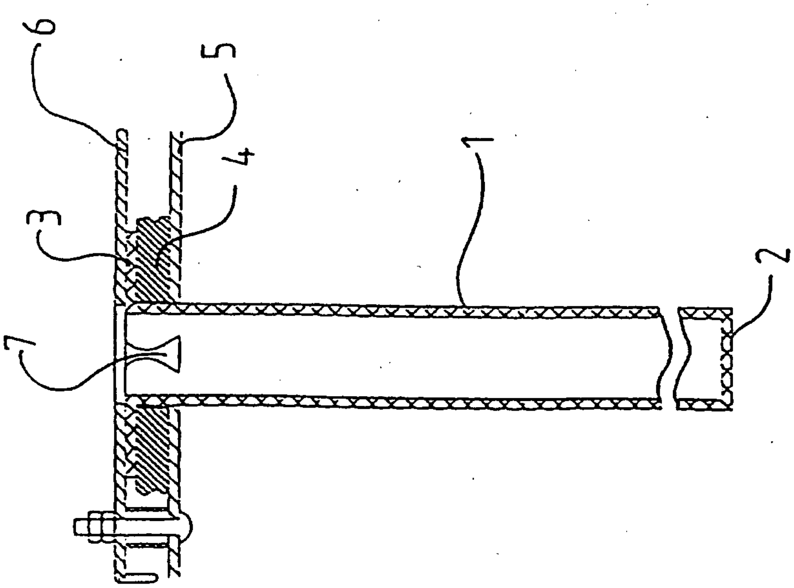
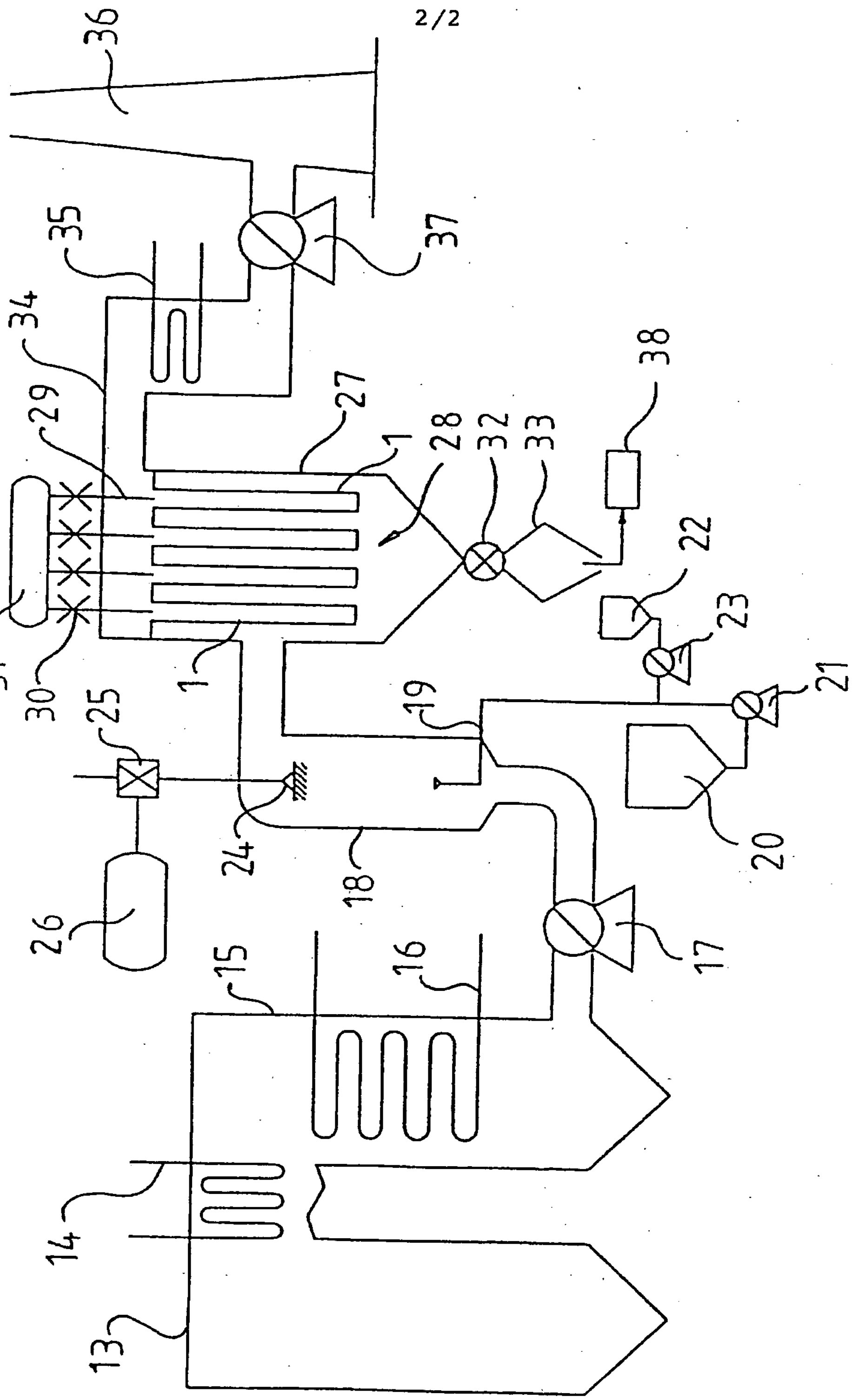



FIG. 1



36
37
35
34
29
27
1
28
32
33
38
22
23
31
30
25
19
21
24
18
20
26
15
16
17
14
13


FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 97/00315

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01D 53/56, F23J 15/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01D, F23J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | EP 0242488 A1 (MITSUBISHI JUKOGYO KABUSHIKI KAISHA), 28 October 1987 (28.10.87) | 1-13 |

--

--------

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"B" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 21 October 1997 | 24.10.97 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Britt-Marie Lundell<br>Telephone No. +46 8 782 25 00 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

01/10/97

International application No.
PCT/DK 97/00315

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0242488 A1 | 28/10/87 | SE 0242488 T3 | |
| | | JP 1924207 C | 25/04/95 |
| | | JP 1924208 C | 25/04/95 |
| | | JP 6049134 B | 29/06/94 |
| | | JP 6049135 B | 29/06/94 |
| | | JP 61111128 A | 29/05/86 |
| | | JP 61111129 A | 29/05/86 |
| | | US 4728503 A | 01/03/88 |